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National Bureau of Standards
Center for Analytical Chemistry
Washington, DC 20234

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Final Report

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This report describes the discovery of laser enhanced ionization in flames along with a description of research on the mechanisms of signal production and collection. Early experiments on the method's use for complex sample analysis are described. Results of this research predict that two photon-two wavelength laser enhanced ionization will produce detection limits at the 10 parts per trillion level in solution for most elements. Laser excitation provides high selectivity so that the method can be predicted to have high accuracy.

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ABSTRACT

This report describes the discovery of laser enhanced ionization in flames along with a description of research on the mechanisms of signal production and collection. Early experiments on the method's use for complex sample analysis are described. Results of this research predict that two photon-two wavelength laser enhanced ionization will produce detection limits at the 10 parts per trillion level in solution for most elements. Laser excitation provides high selectivity so that the method can be predicted to have high accuracy.

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CONTENTS

Abstract iii

Figures v

Tables vi

1. Introduction 1
2. Conclusions 2
3. Recommendations 3
4. Description of the Experimental System 4
5. Preliminary Analytical Results 6
6. LEI Signal Production in Flames 12
7. LEI Signal Collection in Flames 21
8. Use of CW Laser for LEI 26
9. The Future of the LEI Technique 28

References 29

FIGURES

Number		Page
1	Experimental configuration	5
2	Calibration curves for elements in water	7
3	LEI spectrum of Ni-based alloy near the In analysis line (4).	10
4	Processes considered in the theory of LEI signal production	13
5	Comparison of experimental LEI sensitivities to the theoretical sensitivity for twenty-one transitions in fourteen elements (transitions are not identified)	16
6	Partial energy level diagram for Li and detection limits for resonance (670.8 nm), nonresonance (610.4 nm) and two photon transitions 639.3 nm. Limits of detection are 0.001, 0.012, and 0.4 ng/mL	17
7	Stepwise excitation in LEI	19
8	Stepwise excitation of copper with partial energy diagram. .	20
9	Potential (upper) and field (lower) in a flame subjected to an applied potential for three values of the volume ionization rate. Dashed lines indicate effect without a flame . .	22
10	Percent recovery of 10 µg/mL In signal at 303.9 nm vs. sodium concentration using a tungsten plate cathode at -1000 V and -1500 V	24
11	Potential and field behavior in a flame for four applied potentials	25

TABLES

Number		Page
1	Comparison of Detection Limits	8
2	Real Sample Measurements	9
3	LEI Detection Limits (ng/mL) for N_2-pumped and Flashlamp-pumped Dye Lasers	18
4	Limits of Detection for LEI, Comparison of CW and Flashlamp Pumped Dye Lasers	27

SECTION 1

INTRODUCTION

In August 1976 our group was exploring the concentration of atomic species produced in a commercial hollow cathode lamp by observation of laser excited optical fluorescence. Dramatic changes in the voltage of and the current drawn by the cathode were observed when the laser was tuned into resonance with electronic transitions of the species being observed. Transitions producing signals of positive polarity as well as transitions producing signals of negative polarity were observed. The magnitude of the effect was such that transitions of low probability or transitions of high probability but low numbers of atoms were easily observed (1,2).

An attempt was made to observe a similar effect in the flame source of an atomic absorption spectrometer. At the end of the first day of experimentation it was possible to detect a signal from sodium at a concentration of 10^{-9} g/mL in a solution aspirated into the flame. Though the effect was initially not understood, subsequent studies have shown that the technique is generally applicable to many elements and that in the flame, the signal is produced by photon energy augmentation of a collisional ionization process; hence the name laser enhanced ionization.

This report highlights the studies that have been made on this technique, describes its advantages and disadvantages, and indicates its future direction in our laboratory.

SECTION 2

CONCLUSIONS

Laser enhanced ionization (LEI) in flames is a new quantitative analytical spectroscopic method with a number of features that can result in major improvements in accuracy and detectability when compared to existing methods. The basic principle of the use of photons to produce ions selectively has very broad applicability in both inorganic and organic chemical analysis.

LEI in flames has been demonstrated to be successful in analyzing practical samples. The major effort at this stage of the technique's development has been to understand the basic mechanisms of signal collection and production. The signal production mechanism is based upon collisional excitation and ionization accompanied by photon excitation. The theory has been sufficiently developed to allow prediction of experimental detection limits for elemental analysis. Significantly more atomic transitions can be used than in the case of other spectroscopic analyses.

The theory of signal collection has progressed to the point of explaining the phenomenon in terms of the steady state properties of the flame. Alkali metal interference can be reduced in magnitude by producing the laser-generated signal inside of the ion sheath near the cathode. When the signal is produced by ion collection, electrical saturation, even in the CW laser excitation regime, can be observed. This is responsible for the unexpectedly high sensitivity relative to the higher absolute sensitivity of pulsed lasers. A number of "spin-offs" from this research have been identified in the area of flame property measurements such as diffusion coefficients of constituents and flame gas velocity.

Current capabilities indicate part-per-trillion detection limits with minimal interference effects limited primarily by the errors associated with the flame-atom reservoir.

SECTION 3

RECOMMENDATIONS

The laser enhanced ionization method is very new and continued efforts should be put into research on the technique. The following areas should be thoroughly studied before a quantitative technique is established that can be used to analyze a variety of samples with high accuracy:

1. Development of multiphoton stepwise excitation will result in low detection limits for high ionization potential elements as well as providing for higher accuracy through improved selectivity.

2. Modified design of electrodes and optimization of geometry can improve signal collection efficiency as well as reduce interference effects from alkali metals. Improvement of signal-to-noise ratio should be possible.

3. Selection of appropriate laser systems as they become available can improve the ease of use and reliability. Considerable improvement can be made in reproducibility of intensity by using enough power to saturate the transition. Efforts can begin to provide for sequential multi-element analysis.

4. Once these areas have been thoroughly investigated, a quantitative analytical method can be developed and subjected to ruggedness testing and, eventually, round robin tests on environmental samples.

SECTION 4

DESCRIPTION OF THE EXPERIMENTAL SYSTEM

Application of LEI to trace element analysis has been confined totally so far to atmospheric flames. The "analytical burner" is a highly developed and characterized atom reservoir, available commercially from a number of sources. Samples in liquid form are introduced as a fine spray into a laminar pre-mixed flame, in which atomization of the sample occurs. Such a burner with external electrodes bracketing the flame for the ionization measurement is illustrated in Figure 1. The burner is modified by insulating the burner head from the burner body, so that the burner head may also be used as an electrode. The added plates are wired in parallel and are held at high ($\sim$1000 V), negative potential, thus acting as a split cathode. The burner head becomes the anode, from which the background current and signal are drawn. The pulsed (or chopped) current component resulting from the pulsed or chopped cw laser excitation is ac-coupled through a capacitor into a pulse amplification and signal averaging system. The laser beam is directed into the flame and may be conveniently adjusted with a beam director.

Cathode plates are recommended instead of rods for reasons which will be explained later. Also, insertion of uncooled electrodes into the flame is not recommended for analytical purposes because of rapid ($\sim$ minutes-to-hours) degradation of the probes and consequent drift in the measurement sensitivity. For a C_2H_2/air flame supported on a 5 cm slot burner, Mo or W plates separated by $\sim$ 1.0 - 1.5 cm and centered just outside of the width of the flow last indefinitely.

The pre-amplifier design has been described (5). Although signals have been obtained with CW (2), flashlamp-pumped (3-7), and N_2 laser-pumped dye lasers, the flashlamp system producing a 10^{-6}s pulse seems to produce the best sensitivity in atmospheric pressure flames. This is probably due to the $\sim 10^6 s^{-1}$ collisional ionization rates of excited states normally populated by single photon LEI. The bandwidth of the laser is nominally less than the atomic linewidths in the flame.

For flashlamp dye laser excitation, signals are generally averaged at $\sim$15 Hz in a boxcar averager with an effective one second time constant, and the averaged signal is recorded on a strip chart recorder. The laser wavelength may be scanned linearly with time to give a spectral profile on the recorder.

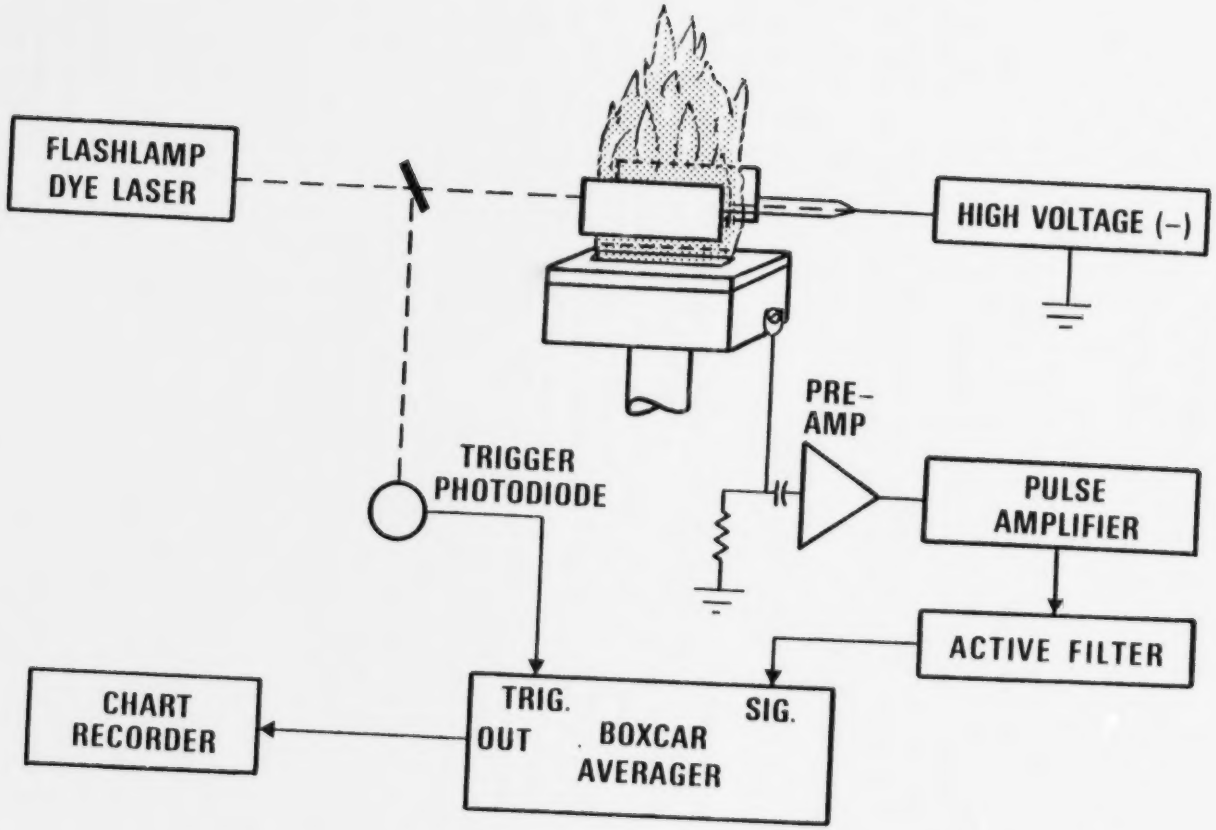


Figure 1. Experimental configuration.

SECTION 5

PRELIMINARY ANALYTICAL RESULTS

Much of the data collected to date with the LEI system must be considered preliminary in the sense that over the past two years a number of new concepts have been discovered about the basic mechanisms governing the operation of the technique. As a result, major changes in the technology have placed the sample measuring aspect in a constant state of change. Nevertheless, it is possible to describe generally the capabilities of the method and to indicate its potential once the major characteristics of the system have been fully analyzed.

DYNAMIC RANGE AND DETECTION LIMITS

The dependence of instrument response on concentration has been determined for neat solutions of 18 elements (using 28 transitions) of which a few are plotted in figure 2. These relationships indicate a linear dynamic range of four to five orders of magnitude, and a widely varying limit of detection which may be correlated with the ionization potential of the element. When compared with other flame techniques, the limit of detection (Table 1) may be seen to vary from orders of magnitude less sensitive (e.g., Cu), to orders of magnitude more sensitive (e.g., Li, In), depending on the ionization potential of the element. Detection limits are reported as that concentration of analyte which yields a signal amplitude three times greater than the noise amplitude observed when the blank solution is aspirated. A more rigorous way of reporting detection limits has been given by Currie (14), but the purpose of Table 1 is to show comparisons with other work not all of which provide sufficient data for the more rigorous analysis. Moreover, the detection limits obtained in neat solutions cannot be expected to be the same for more complex samples. The data show only approximate and relative trends.

The initial instrumental system that has been used to date is capable of making reasonably accurate measurements on those few samples which have been studied. Table 2 illustrates three different types of samples. The measurement of indium in nickel-based alloy, which is a particularly difficult analysis by most other methods, can be made directly using standards of indium dissolved in water. Figure 3 shows a spectrum obtained by scanning the laser. The nickel line at 303.79 nm has very low transition probability and hence is comparable in intensity to the much less abundant indium. It can be seen that the In line at 303.92 is well resolved from other potentially interfering elements.

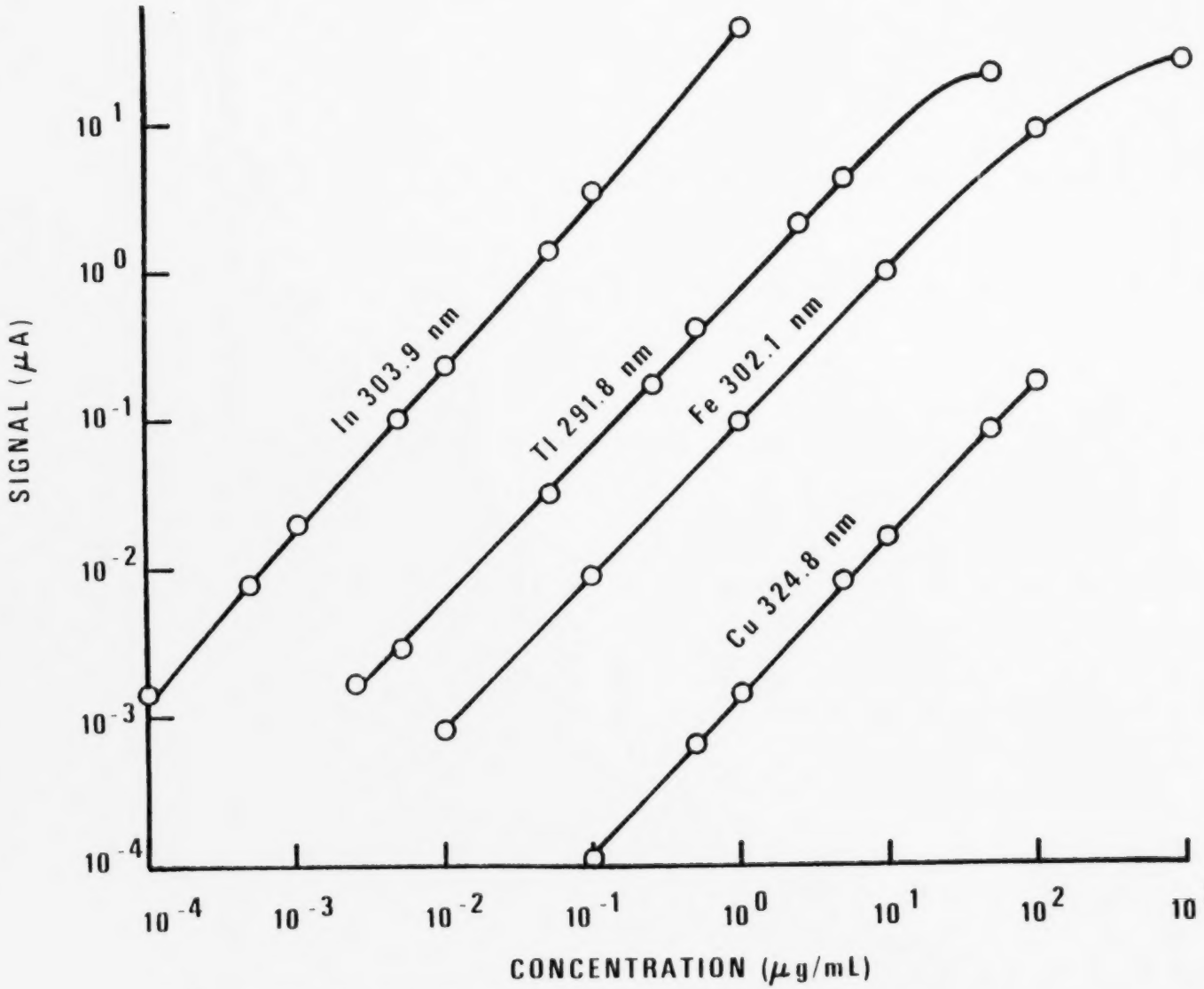


Figure 2. Calibration curves for elements in water.

TABLE 1. COMPARISON OF DETECTION LIMITS (ng/mL)[a].

Element	LEI	FAA[b]	FAE[b]	FAF[b]	LIF[b]
Ag	1	1	2	0.1	4
Ba	0.2	20	1	---	8
Bi	2	50	20000	5	3
Ca	0.1	1	0.1	20	0.08
Cr	2	2	2	5	1
Cu	100	1	0.1	0.5	1
Fe	2	4	5	8	30
Ga	0.07	50	10	10	0.9
In	0.006	30	0.4	100	0.2
K	1	3	0.05	---	---
Li	0.001	1	0.02	---	0.5
Mg	0.1	0.1	5	0.1	0.2
Mn	0.3	0.8	1	1	0.4
Na	0.05	0.8	0.1		0.1
Ni	8	5	20	3	2
Pb	0.6	10	100	10	13
Sn	6	20	100	50	---
Tl	0.09	20	20	8	4

[a]Values taken from references 4 and 10.

[b]Flame atomic absorption (FAA), emission (FAE), fluorescence (FAF) and laser induced fluorescence (LIF) in flames.

TABLE 2. REAL SAMPLE MEASUREMENTS.

Element	Wavelength	Sample	LEI[a]	Expected[a]	Comments
In	303.9	Ni-based Alloy	35	37	1
Mn	304.5	River Sediment	786	770	2
Mn	304.5	SRM 1261-Steel	6700	6600	3

[a] μg/g. Errors approximately 5% relative standard deviation for a single determination.

Comments:

1. No matrix effect; calibration via neat standard solutions.

2. High background current; calibration via standard additions.

3. Moderate background current; matrix effect compensated by using fuel-rich (high electron content) flame for both sample and neat standard solutions.

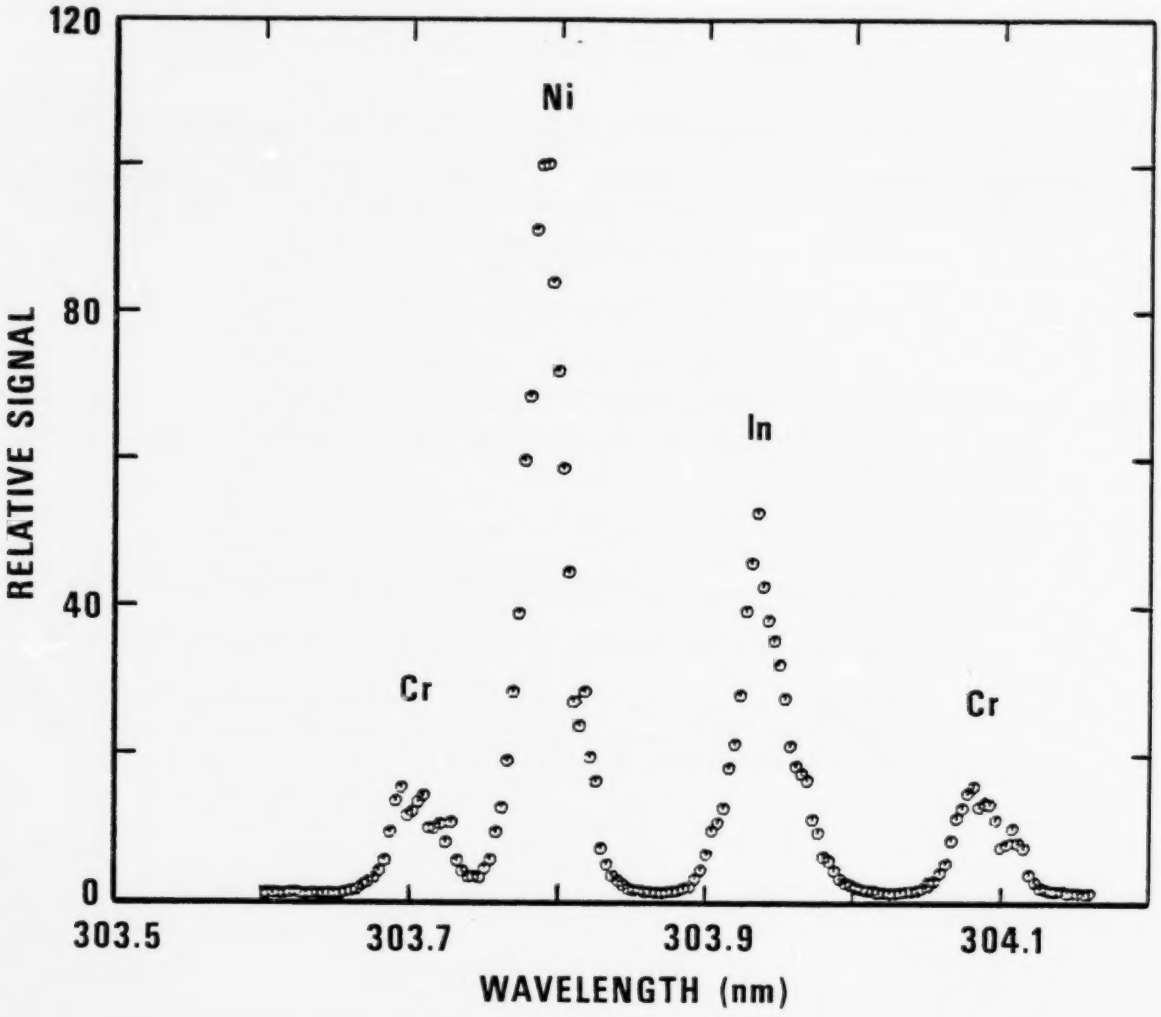


Figure 3. LEI spectrum of Ni-based alloy near the In analysis line (4).

The Standard Reference Material (SRM) 1261 steel was found to produce a slight electrical background; however, it was possible to obtain an accurate signal with neat solution standards using a fuel rich flame. Systematic errors occur when the ion-electron density changes appreciably*. The fuel rich flame increases the ion-electron density to a point where the addition of the steel sample produces no additional effect.

*This subject is treated partially in section 7. Studies subsequent to the period of this report have resulted in electrode designs that eliminate this type of problem.

The river sediment, which produced a rather high background, was accurately analyzed by combining the fuel rich flame composition with a standard additions procedure.

Although many other types of samples need to be analyzed to evaluate the method, there has been sufficient encouragement from the results already obtained to warrant an in-depth study. None of the parameters of the method have been optimized. In fact, on intuitive grounds it seems that the shape and relative position of the electrodes cannot be considered very close to optimum. The best way to arrive at an optimum configuration is to study the basic mechanisms of the method.

The electrical current pulse measured by the detection electronics results from 1) the production of an excess (above the thermal equilibrium value) of ions and electrons in the flame volume illuminated by the laser, and 2) the transport of excess charges through the flame to the electrodes. These distinct aspects of signal generation are referred to hereafter as the "production" and "collection" stages, respectively. Since only the combined effect of both processes is actually observed, simplifying assumptions have been invoked to separate the two for individual study. These assumptions are stated at appropriate points in the following discussions of ion production and collection.

SECTION 6

LEI SIGNAL PRODUCTION IN FLAMES

The detection limit data in Table 1 show a wide variation among the elements studied. We have observed that the detection limit is correlated with the ionization potential of the elements. In the flame there is an ensemble of energetic species, mostly nitrogen, in which energy is transferred by collisional processes. One can calculate the probability of ionization of species in the flame. The energy of the 2500 - 3000 K flame proves to be sufficient to ionize only elements with low ionization potential such as the alkali metals. Thus, the rate of ionization from collisional processes in the flame is low due to the low number density of collision partners with sufficient energy to cause ionization. However, with photon absorption adding energy to the atom, it can be excited to an energy level above its ionization potential.

A diagrammatic representation of the processes considered to be important to the production of charged species in the flame is given in figure 4. The case of a resonance transition is considered for simplicity. The rate constants for the pertinent optical processes of absorption (E_ν B_{12}), spontaneous emission (A_{21}), and stimulated emission (E_ν B_{21}) involve the Einstein coefficients (A and B), and the spectral irradiance of the laser (E_ν). The only collisional processes considered are collisional de-excitation (k_{21}) and collisional ionization from the excited state (k_{2i}). Additional collisional excitation and ionization processes are considered to be of trivial magnitude, and ion-electron recombination is considered to be negligible.

Assuming that the remaining processes are fast with respect to the laser pulse length, the steady state population of the excited state is given by

$$n_2 = \frac{B_{12}\, E_\nu\, (n_T - n_i)}{(B_{12} + B_{21})\, E_\nu + A_{21} + k_{21}} \qquad (1)$$

where n_2, n_T and n_i are the number densities (cm^{-3}) of excited state analyte atoms, total (neutral and ionized) analyte atoms, and ionized analyte atoms, respectively. The rate of ion production ($\dot{n}_i$) from the excited state, E_2, is then

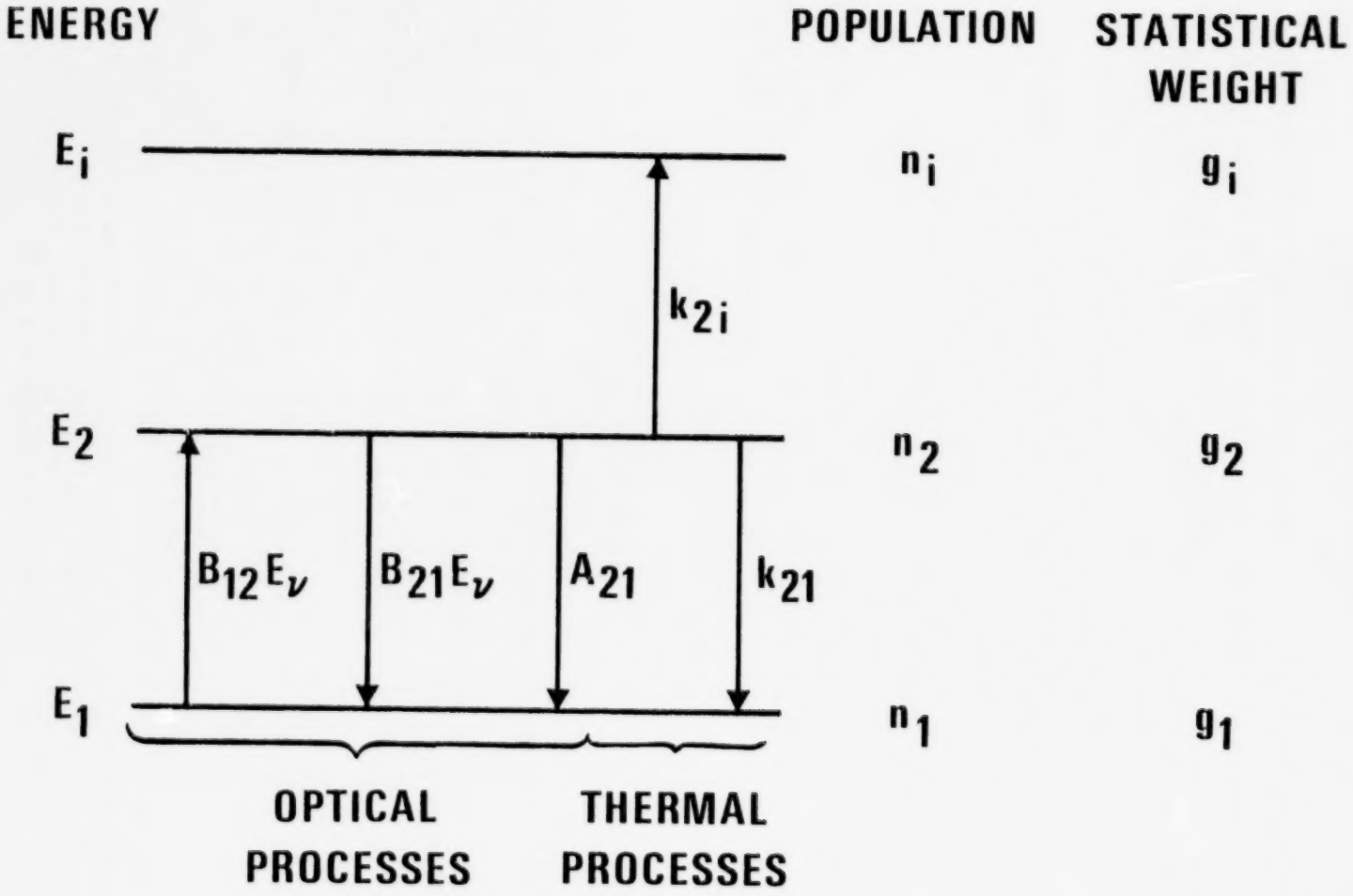


Figure 4. Processes considered in the theory of LEI signal production.

$$\dot{n}_i = k_{2i}\, n_2 = \frac{k_{2i}\, B_{12}\, E_\nu\, (n_T - n_i)}{(B_{12} + B_{21})\, E_\nu + A_{21} + k_{21}} \qquad (2)$$

Note that the rate of production of n_i decreases as n_i increases. As the number of neutral states $(n_T - n_i)$ decreases the rate of production of n_i must decrease. This can lead to saturation of the ionization process. To evaluate equation 2 analytically, one needs to know the functional relationship of E_ν with time, $E_\nu(t)$. To simplify the analysis, it is assumed that $(B_{12} + B_{21})E_\nu << (A_{21} + k_{21})$, that is, optical saturation does not occur.

The time dependent value of n_i is determined by integrating equation (2) and substituting for $N_T - n_i$ in eq. 2 yielding

$$\dot{n}_i = \frac{k_{2i}\, B_{12}\, n_T}{A_{21} + k_{21}}\; E_\nu(t)\; \exp\left\{ -\frac{k_{2i}\, B_{12}}{A_{21} + k_{21}} \int_0^t E_\nu(t')dt' \right\} \qquad (3).$$

The maximum value for the ionization rate is obtained by setting the derivative of equation (3) to zero. By assuming $E_\nu(t) = E_\nu^P\, (t/\tau_p)^x$ where E_ν^P represents the peak spectral irradiance of the laser at τ_p, an empirical expression for the $(\dot{n}_i)_{max}$ is of the form:

$$[\dot{n}_i]_{max} = C_1\, n_T \left[\frac{k_{2i}\, B_{12}\, E_\nu^P}{A_{21} + k_{21}} \right]^{C_2} \qquad (4)$$

where C_1 and C_2 are constants related to the pulse shape, where C_2 is less than or equal to unity, $0 \leq t \leq \tau_p$, $0 \leq x \leq 1$. The nonlinearity of ionization rate with laser irradiance, absorption coefficient, and ionization coefficient (for $C_2 < 1$) reflects the partial conversion of neutrals to ions before the laser peaks in power, and results directly from the appearance of n_i on the right hand side of equation (2). For greater detail consult reference 11.

The ionization rate constant k_{2i} may be shown to have the form

$$k_{2i} = k_0 \exp\left[-(E_i - E_2)/kT\right] \qquad (5)$$

where E_i and E_2 are the ionization potential and excited state energy, k is the Boltzmann constant, and k_0 is a function of temperature (T) (7,12), the masses of the analyte atom and the collision partner (probably N_2 in our flame), the number density of the collision partner, and a collision cross section. For present purposes, the variability of k_0 from one element to the

next is neglected as being much less important than the variability of the exponential term in equation (5). For a 2500 K flame, kT = 1738 cm^{-1}, and each eV (1 eV ≃ 8,000 cm^{-1}) of optical energy increase of the atom may be seen from equation (4) to increase the ionization rate constant by a factor of exp [8000/1738] ≃ 10^2. Photons from a doubled dye laser range from about 2 to 5 eV, for implied ionization enhancements of 4 to 10 orders of magnitude. Of course, saturation effects may place a limit to this range.

If a number of simplifying assumptions are made (11), expected signal levels for a number of transitions for the elements can be calculated. Figure 5 is a correlation plot of the calculated vs. experimental signal. Although a good deal of scatter is observed, the correlation is clearly present.

For a given photon energy one can see that those elements with the lower E_i have a larger rate constant, or conversely, if we can add energy via photon absorption, the rate constant can be increased exponentially at 10^2/eV of difference in E_i-E_2.

An interesting example solidifies these points and provides some insight into the method. Inspection of the partial energy level diagram for lithium (figure 6) indicates that the rate constant for ionization by thermal excitation (dashed lines; solid line is photoexcitation) is exp[(31,283 - 14,904)/1738] ∿1.2 x 10^4 times larger from the ^2D level than from the $^2P°$ level. However, the population of the $^2P°$ state by thermal excitation is exp(-14,904/1738) ∿ 2 x 10^{-4} that produced by photoexcitation assuming comparable cross sections for photoexcitation. This means that the detection limits by either excitation process should be comparable which is experimentally proven to be so within a factor of 10.

The impact of the above for chemical analysis is that, for many elements, infrequently used optical transitions will produce large signals in LEI. This means that there will be a few more lines that can cause interferences. On the other hand it may allow the analytical spectroscopist to use alternate lines more conveniently than with other spectroscopies when an overlap of an interfering line with the normally used line occurs.

A more attractive possibility exists in the use of two-photon excitation. If one uses one wavelength (such as 639.3 nm for lithium in figure 6), two photon excitation must couple with a virtual state and suffer the loss in cross-section for this event to occur. On the other hand if two different wavelengths are used and each wavelength excites to a real level, two benefits are gained. First the selectivity of the photoexcitation process increases by the product of the selectivity factors for each wavelength. Second, the cross sections are much higher than the virtual level two-photon excitation. Two UV photons — from a suitably high-powered frequency-doubled laser — could be used to excite energy levels up to ∿10 eV above the ground state. The effective single-photon wavelength of such transitions is in the vacuum UV. Therefore, one can avoid the usual experimental difficulties and still excite very high energy levels.

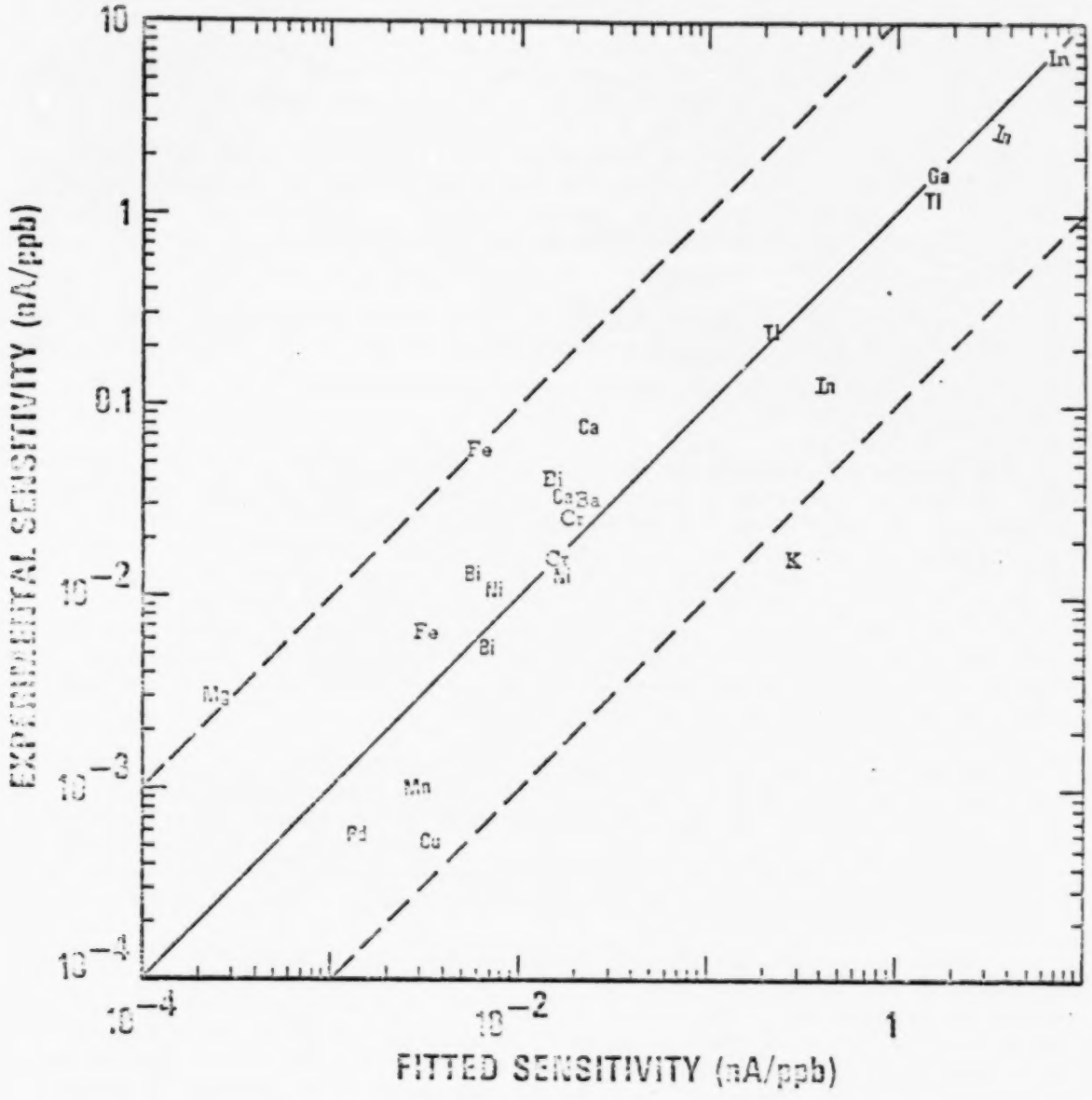


Figure 5. Comparison of experimental LEI sensitivities to the two-parameter theoretical fit value for twenty-one transitions in fourteen elements. The dashed lines are set at a factor of 10 away from the center line. Different values for the same element are for different optical transitions.

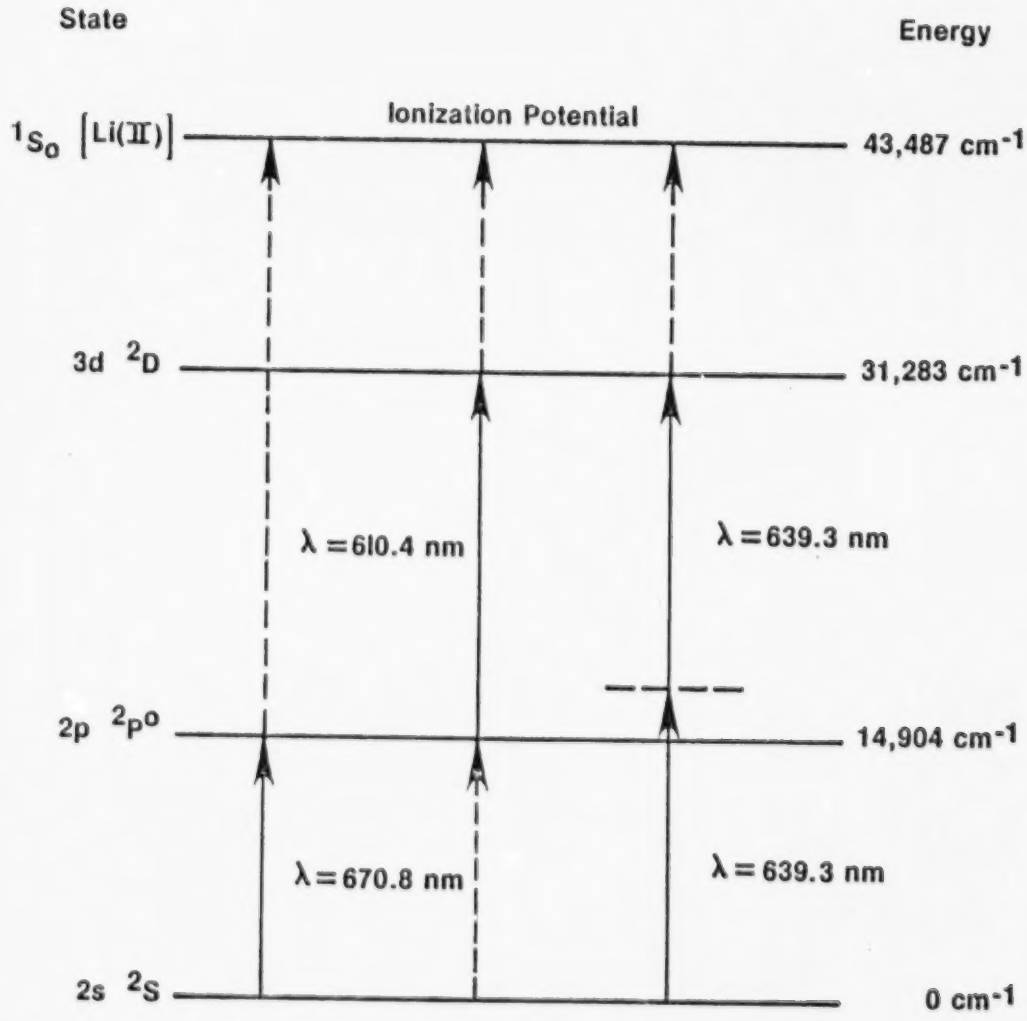


Figure 6. Partial energy level diagram for Li and detection limits for resonance (670.8 nm), nonresonance (610.4 nm) and two photon transitions 639.3 nm. Limits of detection are 0.001, 0.012, and 0.4 ng/mL.

Using instrumentation made available at the NBS Center for Fire Research, the first LEI experiments using multiple wavelength, stepwise photoexcitation were performed. A single nitrogen laser was used to pump two tunable dye lasers. The two dye laser beams were directed colinearly through a pre-mixed air-H_2 flame, and LEI was detected in the usual manner (9).

Figure 7 summarizes the results obtained using both single and dual wavelength N_2 pumped dye laser excitation for several elements. The sensitivity enhancement factors resulting from the second step of laser excitation range from 1 to 3 orders of magnitude. A variety of both instrumental and fundamental parameters determine the degree of enhancement achieved including: the power of each laser; the degree of optical and electrical saturation involved for each transition; the photon energies; the ionization potential; and the transition strengths of each line.

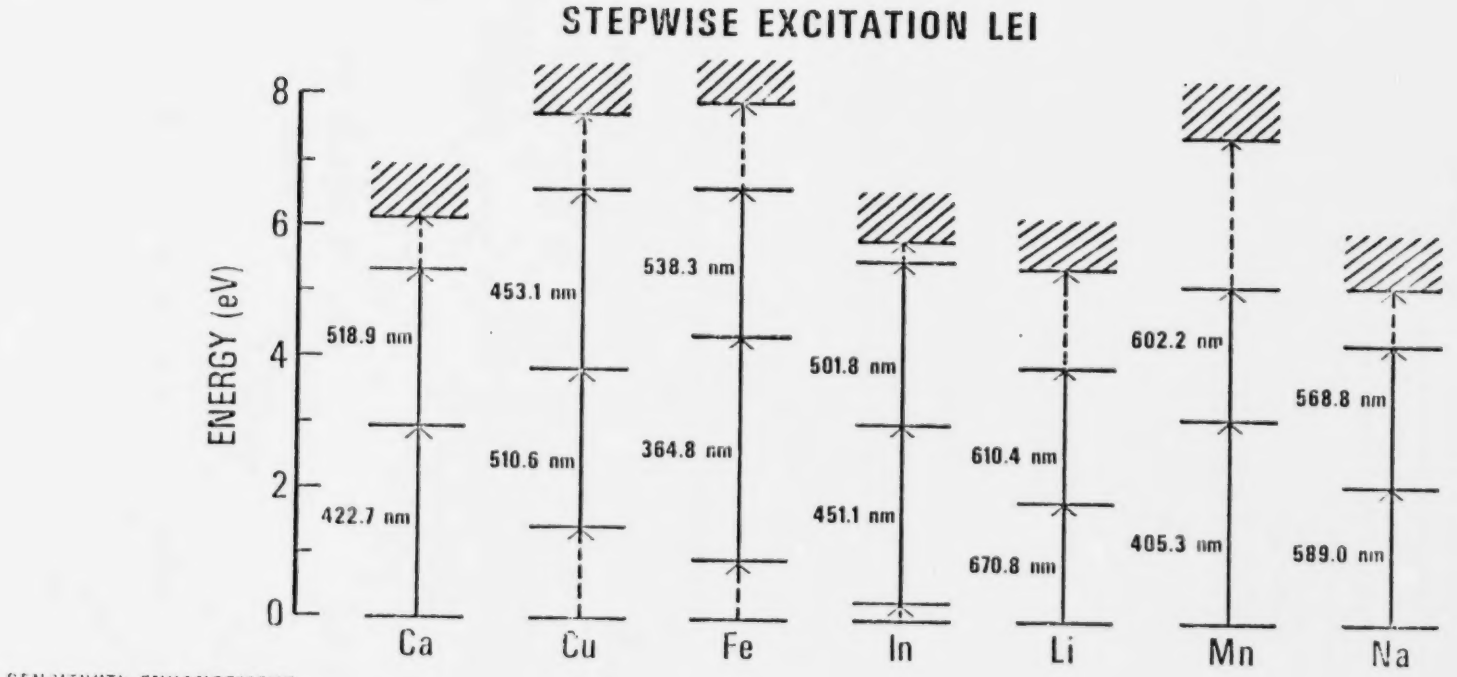
However, as Table 3 shows, despite the sensitivity enhancements, the detection limits obtained are, with the exception of sodium, inferior to those reported earlier for LEI using single photon LEI with a flashlamp pumped dye laser.

TABLE 3. LEI DETECTION LIMITS (ng/mL) FOR N_2-PUMPED AND FLASHLAMP-PUMPED DYE LASERS.

Element	N_2 Laser[a] Single Wavelength	Dual Wavelength	Flashlamp
Ca	30,000	100	0.1
Cu	> 10^6	500	100
Fe	2,000	100	2
In	100	0.6	0.006
Li	4	0.04	0.001
Mn	30	5	0.3
Na	6	0.04	0.05

[a]Taken from reference (9).

This observation is consistent with preliminary studies on the time dependence of signal production and collection. Production suffers when the characteristic excited state ionization time, $1/k_{2i}$, is much longer than the pulse length. Also, the obtainable peak current suffers when the time required to extract an ion from the flame is longer than the laser pulse, as is discussed in more detail in the next section.



	Ca	Cu	Fe	In	Li	Mn	Na
SENSITIVITY ENHANCEMENT RESULTING FROM SECOND PHOTON	270	>1600	20	250	100	7	690
DETECTION LIMIT (ng/ml)							
SINGLE LASER	30,000	$>10^6$	2,000	100	4	30	6
DUAL LASER	100	500	100	0.6	0.04	5	0.04

Figure 7. Stepwise excitation in LEI.

An attempt was made to use two flashlamp pumped dye lasers which produce a 1 μs pulse. Figure 8 depicts a partial energy diagram of copper. Radiation at λ_1 was produced by a Chromatix Corp. model CMX-4* flashlamp pumped dye laser while radiation at λ_2 was produced by a Phase-R Corp. model DL-1400* flashlamp pumped dye laser. Both lasers were fired synchronously. The sensitivity (slope of the calibration curve) of the technique is about 10^2 times greater when the stepwise excitation is done than when only one wavelength is used. This improvement did not carry over to a similar improvement in detection limit because of an inordinate amount of radiofrequency interference. This reduced the improvement in limit of detection to a factor of 25.

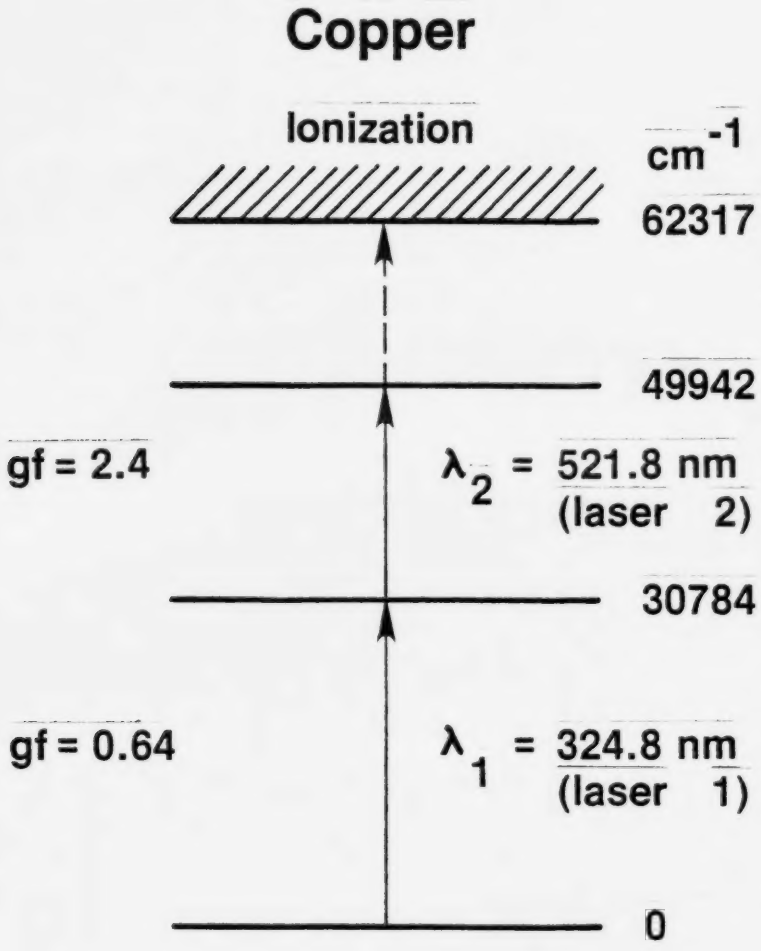


Figure 8. Stepwise excitation of copper with partial energy diagram.

*See disclaimer on page ii.

SECTION 7

LEI SIGNAL COLLECTION IN FLAMES

To begin the description of the signal collection process, it is important to describe the properties of a flame when a potential is applied between electrodes within or in close contact with the flame. The response of flames to external fields has been extensively studied and documented by Lawton and Weinberg (12). At the instant a field is applied to a flame, electrons and positive ions begin to move toward opposite electrodes with different drift velocities (V), given by

$$V_e = -\mu_e E$$
$$V_i = \mu_i E \qquad (5)$$

where E is the electric field, μ the species "mobility", and the subscripts distinguish electrons (e) and positive ions (i). The mobility depends inversely on mass, and is thus much greater for electrons than positive ions. Since electrons and ions are generated at the same rate in the flames, the greater electron extraction rate results in a build-up of net positive charge in the flame. This charge is localized around the cathode, and continues to build up until the negative potential of the cathode is effectively neutralized beyond the net positive charge cloud. The net positive charge region around the cathode is called the "sheath" or "cathode fall". The latter designation refers to the fact that virtually the entire potential difference between the cathode and anode is "dropped" across the sheath.

Figure 9 illustrates the behavior of the potential and the field in three idealized flames of uniform temperature and composition between plane parallel electrodes, with a "sub-saturation" negative potential applied to the cathode (12). The term saturation refers to the condition where there is no field free region between the electrodes. The dashed lines represent the behavior of the potential (upper line) and field (lower line) in the absence of a flame. The solid lines show the effect on the potential and field of three flames which differ in volume ionization rate, r_i (ions produced per cm^3 per second). This rate is a function of the temperature and composition of the flame as well as aspirated ionizable species such as K, Na, etc. The sheath is the region of non-zero field and non-constant potential, i.e., to the right of the vertical line. Between the anode and the edge of the sheath, no field exists, and the potential takes on the value of the anode potential (zero, for a grounded anode). Therefore, a laser beam placed in the region to the left of the boundary (using condition B) in figure 9 will

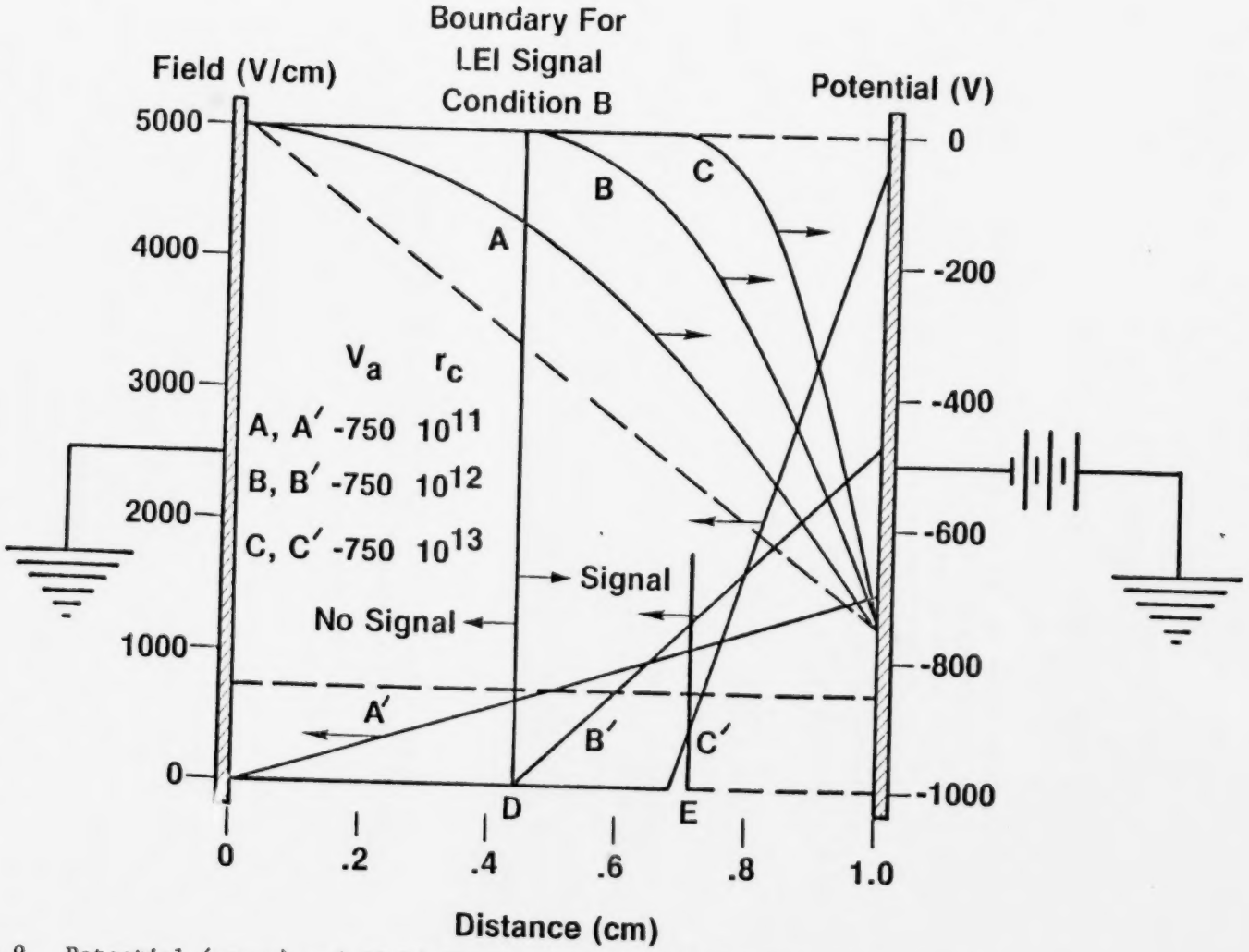


Figure 9. Potential (upper) and field (lower) in a flame subjected to an applied potential for three values of the volume ionization rate. Dashed lines indicate effect without a flame.

produce ions and electrons, but no signal will be observed at the electrodes. Furthermore, for a given laser beam position between the electrodes which currently gives a signal, an increase in r_i, for example caused by an increased concentration of an alkali metal, may cause a decrease in signal intensity. This is observed experimentally. Figure 10 shows a substantial decrease in signal above 200 μg/mL matrix sodium concentration. The reader will note a considerable enhancement in signal at intermediate concentrations of sodium. The cause of this has not been completely verified, but current data suggest that it results from the position in the flame that the signal is generated which is consistent with the foregoing discussion. For example, the position marked E in figure 9 suggests a maximum in the curve as shown in figure 10. A number of experiments have been performed in an attempt to reduce this alkali metals interference effect. Major improvements have been realized by making it possible for the laser active volume to exist within the sheath. Electrodes in the shape of rods cause the LEI signal to be more affected than parallel plates. This is because the field gradient is larger which produces a narrower sheath or region where the laser signal can be collected than with flat plates. A recent improvement has been made by placing a water-cooled electrode in the flame. Close proximity of the laser beam to the electrode allows the laser signal to be produced within the small sheath that is generated at high alkali metal concentrations [approx. 5 mg/mL (13)]. Increasing the voltage between the plates up to breakdown in the plasma also helps by increasing the size of the sheath. This can be seen in figure 11 which shows calculations of field and potential for different voltages.

A number of diagnostic techniques have been developed that provide data on a number of the basic processes in the LEI signal production and collection. For example, it has been found possible to measure an image of the laser-produced ion cluster which generates a signal as it is collected on the cathode (13). From this and similar techniques it may be possible to measure a number of electromigration properties of species in a flame, such as diffusion coefficients and velocities of gaseous species. It has even been possible to observe LEI of certain molecular species in the flame (8).

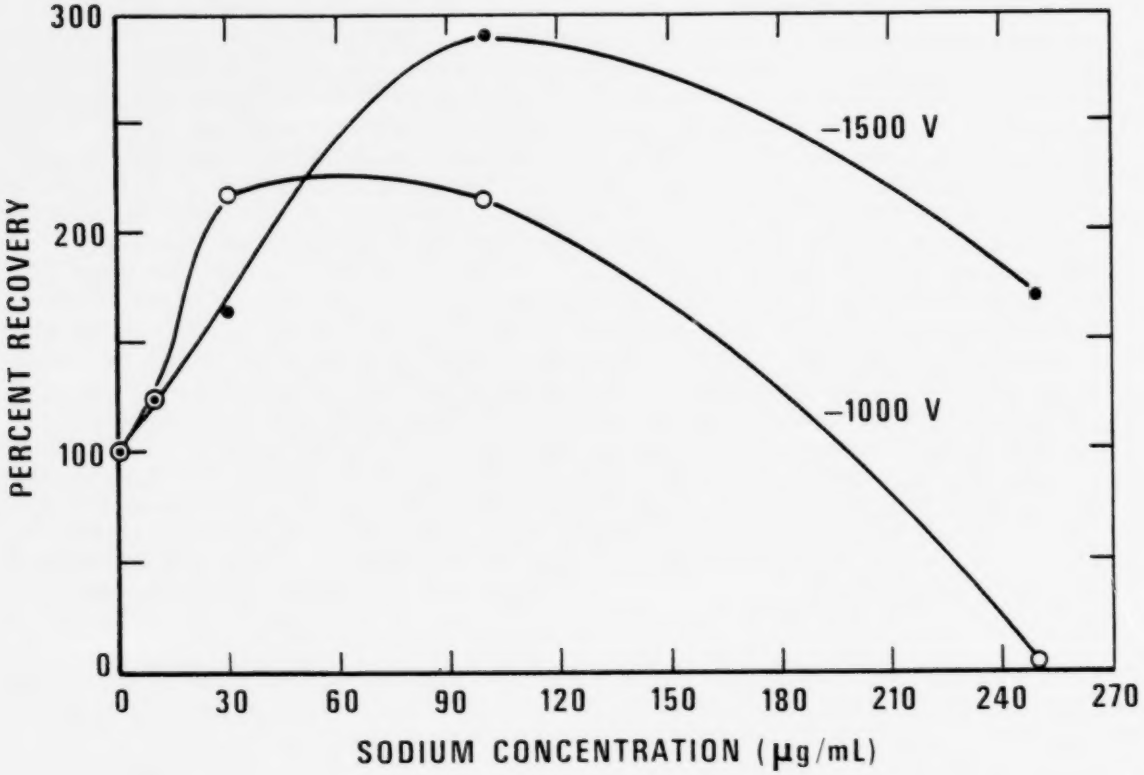


Figure 10. Percent recovery of 10 µg/mL In signal at 303.9 nm vs. sodium concentration using a tungsten plate cathode at -1000 V and -1500 V.

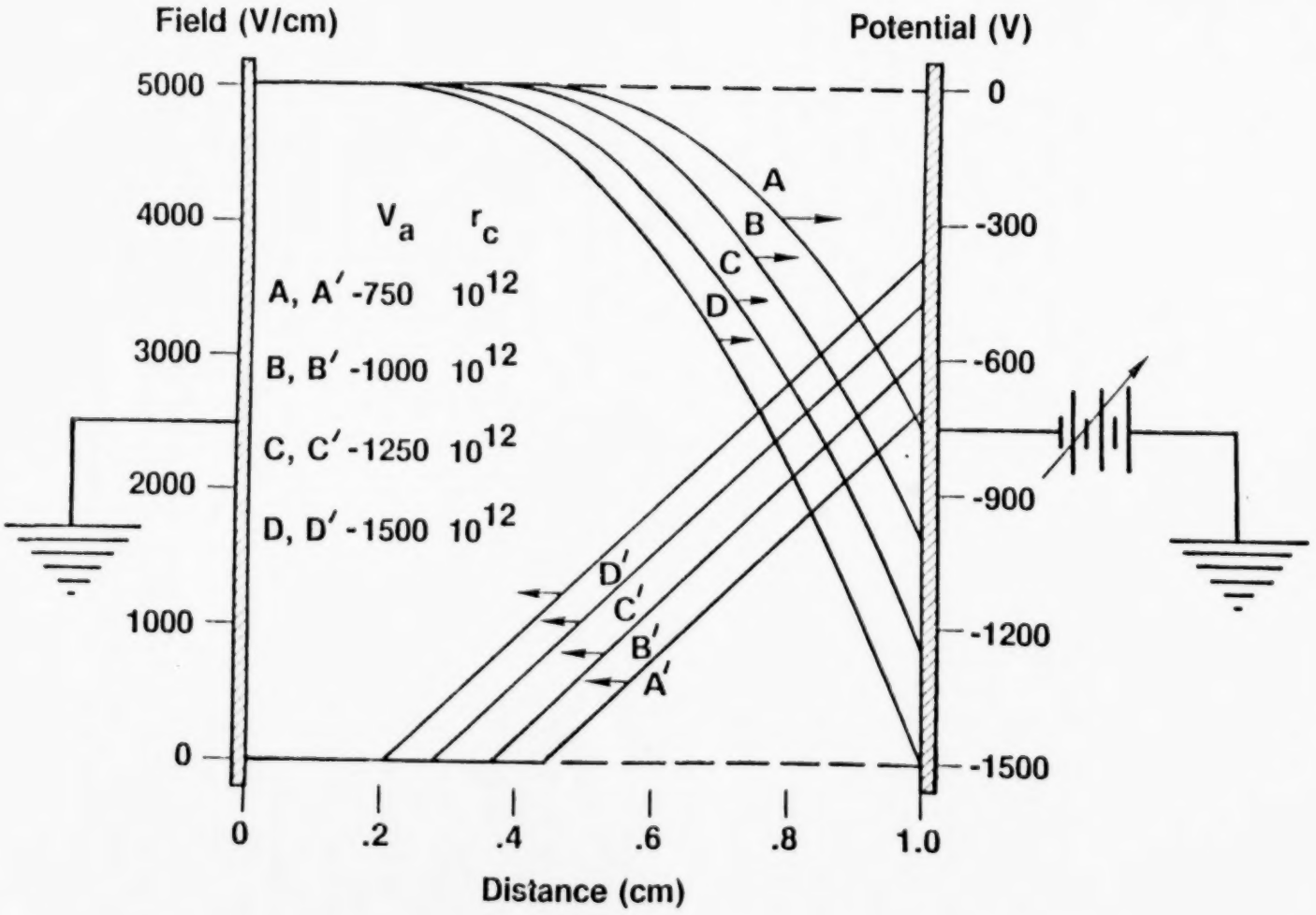


Figure 11. Potential and field behavior in a flame for four applied potentials.

SECTION 8

USE OF CW LASER FOR LEI

The initial experiment on LEI four years ago was done using a continuous wave (CW) argon-ion-laser-pumped, dye laser. Such lasers possess a number of attractive features when compared to pulsed laser systems. Among these are: high average power, high stability of both wavelength and intensity, laser signal processing requiring less sophisticated electronics, and the ability to modulate the wavelength. However, the use of these lasers has been limited by the relatively narrow wavelength range over which they have operated. With a 5 W argon ion laser system only Na and Ba could be measured, and for this reason the majority of LEI research has been done using pulsed laser systems. In addition, the CW laser provides an equilibrium condition not possible with pulsed lasers (except on us time frames). This enhances comparison of theory with experiment and has proven to be most useful in developing the diagnostic technique mentioned in the previous section.

With the goal in mind of obtaining wavelength coverage from 407 to 750 nm, a 6 W, krypton-ion-laser-pumped, dye-laser system was assembled. The laser beam is mechanically chopped and the signal is detected using a lock-in amplifier. Excellent linear dynamic range has been demonstrated for three elements. Detection limits have been measured for seven elements and are presented in Table 4 along with corresponding detection limits for LEI using the flashlamp pulsed dye laser. With the exception of Na, the LEI detection limits obtained with the CW laser do not compare favorably with those for the flashlamp laser. This may be due in large part to the lower photon energies (higher wavelengths) being utilized for the CW measurements. In the only case where the same wavelength has been used for both lasers, Na at 589.0 nm, the CW detection limit (0.025 ng/mL) is better by a factor of four than that of the flashlamp laser. Since the peak power of the flashlamp laser is 10^6 times the average power of the CW laser, one might wonder how the limits of detection can be comparable. Recent data have shown that with the CW laser, the relatively long time available for both signal production and collection makes it possible to observe saturation of LEI at the low power of the CW laser (13).

The CW LEI method has much merit for chemical analysis. The wavelength and intensity can be kept more stable than pulsed lasers. Both amplitude and frequency modulation can be used to enhance the signal to noise ratio and reduce the magnitude of the background.

TABLE 4. LIMITS OF DETECTION FOR LEI. COMPARISON OF CW AND FLASHLAMP PUMPED DYE LASER.

Element	CW		Flashlamp	
	ng/mL	(wavelength) nm	ng/mL	(wavelength) nm
Ca	1	(422.7)	0.1	(300.7)
Ga	300	(417.2)	0.07	(287.4)
In	0.1	(451.1)	0.006	(303.9)
Li	20	(460.3)	0.001	(670.8)
Rb	16	(420.2)		
Na	0.025	(589.0)	0.1	(589.0)
Sr	4	(460.3)		

SECTION 9

THE FUTURE OF THE LEI TECHNIQUE

The LEI technique has the potential for the detection and quantification of most of the elements at or below the part-per-trillion level with high selectivity and accuracy. The technique already appears to be a substantial improvement over competing techniques, and therefore, more research should be conducted.

Research on the signal production and collection processes will result in urther improvements in the design of the system. The use of two photon excitation where each photon populates a resonance energy level in the atom can greatly enhance the sensitivity and selectivity of the technique. While the flame is the best medium for LEI at the present time, future research on atom reservoirs such as vaporization of solids into a gaseous discharge may be of interest for LEI.

Significant insight has been obtained on the basic processes of the LEI technique. After several of the above mentioned areas have been studied, a number of developments need to be made to result in a quantitative analytical instrument. For example, multiple element capability might be investigated by using jump tuning of the laser system. In addition, the technique needs to be evaluated for sources of error including ruggedness, reproducibility, and accuracy.

To date, our studies indicate that LEI is an important analytical technique because of its sensitivity and specificity for the analysis of trace constituents.

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